Environmental Science & Technology

Article

pubs.acs.org/est

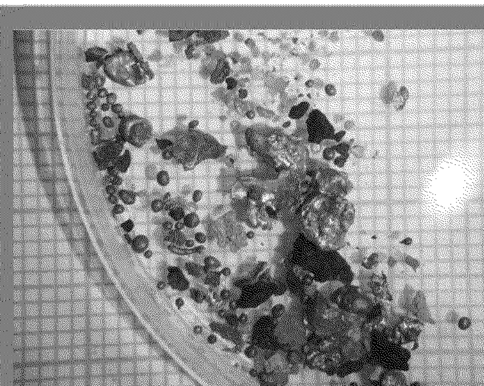
Pb Particles from Tap Water: Bioaccessibility and Contribution to Child Exposure

Elise Deshommes*,† and Michèle Prévost†

†Ecole Polytechnique de Montreal, NSERC Industrial Chair on Drinking Water, CGM Department, C.P. 6079 succ. A, Montreal (QC) H3C 3A7, Canada

* Supporting Information

High particulate lead (Pb) levels can be measured in tap water, but the hazard linked to particulate Pb ingestion is unknown. An in vitro test was developed to determine the bioaccessibility of Pb particles from tap water, based on the Relative Bioaccessibility Leaching Procedure validated for soils, and applied to lab-generated particles and field particles collected behind the aerator tap. Field particles were found in 43% of the 342 taps investigated equipped with an aerator, and contained significant amounts of Pb (0.003−71%, median 4.7%). The bioaccessibility of lab-generated particles ranged from 2 to 96% depending on the particle type (Pb(II) > Brass > Pb(IV) > solder), while that of field particles was distributed between 1.5 and 100% (median 41%). The hazard of particulate Pb ingestion depends on the amount and concentration ingested, and the bioaccessibility of the particulate Pb forms involved. Using the Integrated Exposure Uptake Biokinetic model, the impact of particulate Pb on the exposure of children aged 0.5−7 for the distribution system studied was the most significant when considering a fraction of the exposure from large buildings.



INTRODUCTION

Although blood lead levels (BLLs) have been steadily declining for decades, exposure from residual sources must be reduced, since the current guideline of 10 μg/dL is under review.[1,2] In fact, no safe threshold can be established, now that irreversible neuro-developmental effects have been measured in children at BLLs < 5 μg/dL.[3,4] Tap water is a significant remaining contributor to BLLs,[5,6] through many sources: numerous lead service lines (LSLs) are still in place in North America, which can result in long-term Pb deposits in premise piping (PP);[7] there is a legacy of Pb-containing materials in PP; brass fixtures and faucets can contain up to 8% Pb; and solders with 40−50% Pb content can still be found in an estimated 81 million U.S. homes.[8,9] The contribution of particulate Pb to the total Pb exposure from tap water is unknown. It could be considerable, as very high Pb levels in tap water that may indicate a significant fraction of Pb particles, have been linked to high BLLs in children.[10,11] In order to assess the scale of this exposure, more information is needed about the occurrence and bioavailability of particulate Pb.

Drinking water regulations generally require the determination of total Pb, which includes a fraction of soluble Pb (<0.1 μm), and an easily dissolved fraction of colloidal and particulate Pb (≥0.1 μm). However, particulate Pb can be underestimated. In fact, the historical acidification standard of 0.15% HNO_3 for metal analysis will dissolve most Pb colloids and particles; however, a more stringent digestion is needed to make some Pb forms soluble.[12,13] Also, even though dangerously high concentrations are fairly rare in data obtained with standard protocols, particulate Pb can often occur at significant concentrations at the tap.[14] Moreover, current sampling protocols performed at a low flow rate, or preceded by system flushing, may not reflect the levels to which consumers are exposed.[14] Early reports of Pb release from solders and brass fixtures in a new large building show that particulates >0.2 μm can contribute significantly to Pb levels at the tap.[12] In Montreal, up to 1617 μg/L of particulate Pb (>0.45 μm) has been recorded in houses supplied by a LSL, and the concentrations increased considerably when samples were collected with repeated, rapid, on/off faucet action at high flow rates.[14,15] In another study, consistently high particulate Pb levels (maximum 912 μg/L) were measured in a large building complex (>0.45 μm).[16] Large buildings may be prone to particulate Pb release owing to large volumes of PP, which are often associated with long stagnation times. This raises special concern for schools and daycare centers, as their populations are the most vulnerable to Pb effects.

Finally, the impact of particulate Pb ingestion on BLLs can only be evaluated if the bioavailability of the Pb contained in the particles present at the tap is assessed. That impact depends on multiple factors related to their dissolution in the stomach, such as the particle matrix and size.[17,18] The in vitro bioaccessibility (IVBA) of Pb particles is the fraction of Pb

Received: December 19, 2011
Revised: April 15, 2012
Accepted: April 27, 2012
Published: April 27, 2012

   dx.doi.org/10.1021/es2045585 | Environ. Sci. Technol. 2012, 46, 6269−6277

that dissolves under simulated gastro-intestinal digestion conditions, and becomes available for absorption into the systemic circulation through the intestinal wall.[17] IVBA assays have mainly been developed to evaluate scenario where children aged 2−3 are exposed to soil Pb particles due to hand-to-mouth activity.[17] Some of the many in vitro protocols developed have been validated with in vivo data on animals, piglets being recognized as the animal model best suited to represent the child's digestive system.[19] The Relative Bioaccessibility Leaching Procedure (RBALP), described by Drexler and Brattin, is one of these tests that was fully validated.[18,20]

The objectives of this study are as follows: (1) to develop an in vitro test to measure the IVBA of Pb particles from tap water; (2) to establish the IVBA of Pb in lab-generated and field-collected particles (substitute for particulate Pb); and (3) to evaluate the contribution of particulate Pb to the exposure of children aged 0.5−7 using the Integrated Exposure Uptake Biokinetic model for Pb in children (IEUBK).

MATERIALS AND METHODS

In Vitro Protocol. An IVBA assay for drinking water particles was developed based on the RBALP.[20] Modifications were performed, but not on parameters recognized to affect IVBA measurements (Supporting Information, SI). All of the materials used were either metal-free or soaked for at least 24 h in a 10% HNO_3 bath (trace metal grade), rinsed with ultra pure water, and dried in a Pb-free environment. A synthetic gastric fluid (0.4 M glycine and ultra pure HCl) was adjusted to pH 1.5 ± 0.05 with HCl at 37 °C on the day of the experiment. A volume of gastric fluid was then added to the bulk particle mass previously weighed in a 15 mL tube (0.01−0.08 g), so that the S/L ratio was equivalent to 1 g of particles for 200 mL of fluid for field particles, and from 1/100 to 1/200 $g \cdot mL^{-1}$ for lab-generated particles. The mixture was agitated end-over-end at 28 ± 2 rpm in an incubator at 37 °C. After 1 h, it was filtered on a 0.45 μm cellulose acetate filter using a vacuum device (at least 6 rinses). The filtrate was collected in a receptor tube and diluted to 50 mL. The filter was collected and subjected to aqua regia digestion (4.5 mL ultra pure HNO_3 + 1.5 mL ultra pure HCl; 15 min; 1000 W; 220 °C) using a microwave lab station (Ethos Series, Milestone). Digested samples were acidified within 12 h with at least 0.5% HNO_3 and 0.5% HCl (ultra pure). Analyses were carried out with an ICP-MS (Agilent, 7500ce), mostly within 30 days. Metal detection limits were as follows: 0.2 μg Pb/L, 0.6 μg Cu/L, 1 μg Sn/L, 3 μg Zn/L, 10 μg Fe/L, and 50 μg Ca/L. If an insoluble solid remained following microwave digestion, then it was isolated, weighed if possible, and analyzed by X-ray diffraction (XRD, Bruker D8-Discover, reflection θ/θ, radiation $CuK\alpha_1$, λ = 1.54056 Å). Mass balances were performed using Pb reference materials. The high recoveries for these reference materials (68−106%) are indicative of the value of the adapted RBALP (SI). During the in vitro digestion, a blank was performed every 10 samples, and the pH of the mixture was checked after 1 h every 10 samples, so that pH remained <2. During microwave digestion, a blank and a control (Pb or multimetal solution) were added to each batch. The IVBA was calculated as follows:

$$\mathrm{IVBA}(\%) = \frac{\text{total Pb (filtrate)}}{\text{total Pb (filtrate + filter)}} \times 100$$

$$\begin{aligned} &\mathrm{IVBA}\ (\mathrm{mgPb/gbulkparticles}) \\ &= \mathrm{IVBA}\ (\mathrm{mgPb/g}) \\ &= \frac{\text{mgPb (filtrate)}}{\text{g of bulk particles}} \end{aligned}$$

Lab-Generated Particles. Five types of particles potentially present in tap water were generated in the laboratory: solder particles (~1 mm) from a 50/50 Pb−Sn solder wire (Alfa-Aesar); brass "chips" (~50 μm-2 mm) from two ball valves (one of NSF-certified yellow brass (Y-brass), the other of red brass (R-brass) using a small drill bit); a Pb(II)-based scale deposit scratched from an LSL collected in Montreal, which composition is detailed in Deshommes et al;[14] and Pb(IV) particles <250 μm (PbO_2, Alfa-Aesar).

Field-Collected Particles. Particles trapped behind the tap aerator in 351 homes from several boroughs throughout the city of Montreal were collected,[14,21] and in a large building complex near Montreal (45 taps, 12 buildings).[16] The homes were categorized as follows: 216 with an LSL, 127 without an LSL, and 8 "probably" having an LSL (not confirmed). Fifty-eight percent of the taps sampled in the large buildings and 8% of the kitchen taps in the homes did not have an aerator, and the aerators on some taps could not be removed. A total of 88 samples were collected from the homes with an LSL (41%), 44 samples from homes without an LSL (35%), 4 samples from homes "probably" having an LSL, and 10 samples from large buildings, mostly behind the kitchen tap aerators. Photographs were taken of all of the samples collected. Forty-two samples with sufficient mass (0.01−0.08 g) were used directly. Sets of particles <0.01 g were mixed per housing category, and 10 random subsamples of 0.02−0.06 g were constituted and tested for their IVBA. Sets of particles >0.08 g were fractioned randomly, and 13 subsamples were tested (SI). Finally, one of the aerator taps sampled presented a significant number of solder and iron corrosion particles. These particles were segregated, grouped by size category for each speciation, and each group was tested for its IVBA.

IEUBK Simulations. Version IEUBKwin1.1_Build11 was used to estimate the BLLs for children aged 0.5−7. Lead exposure from tap water, soil, dust, air, and diet was considered. Dissolved and particulate Pb concentrations applied for tap water were a combination of those measured in homes with an LSL in Montreal[14,15,22] (random daytime · RDT and 5-min flushing samplings) and in large buildings close to Montreal[16] (1st flush). To take into account occurrence and absorption differences for dissolved and particulate Pb, the following steps were followed to produce the total Pb input to the model:

Estimate relative particulate Pb bioavailability (RBA) from its measured IVBA%, using the in vivo−in vitro relationship of Drexler and Brattin:[20]

$$\mathrm{RBA}_{\%} = 0.878 \times \mathrm{IVBA}_{\%} - 0.028$$

Adjust the particulate Pb fraction in the total Pb concentration input by multiplying it by its estimated RBA%, and dividing it by the default RBA of 50% applied by IEUBK for total Pb:

$$\mathrm{Pb}_{\mathrm{total}\ \mu g \cdot L^{-1}} = \mathrm{Pb}_{\mathrm{dissolved}\ \mu g \cdot L^{-1}} + \left[\mathrm{Pb}_{\mathrm{particulate}\ \mu g \cdot L^{-1}} \times \frac{\mathrm{RBA}_{\%}}{50_{\%}} \right]$$

dx.doi.org/10.1021/es2045585 | Environ. Sci. Technol. 2012, 46, 6269−6277

Table 1. Description and Justification of the Inputs to the IEUBK Simulations

	AGE CATEGORY (yrs)	0-1	1-2	2-3	3-4	4-5	5-6	6-7	JUSTIFICATION
DRINKING WATER	Drinking water intake — L/d	0.742	0.91	0.91	0.91	1	1	1	Values used by Montreal Public Health authorities[23]
	RDT concentration[a] in LSL houses — μg Pb/L				Median soluble Pb: 17; Median (10th-95th percentile) particulate Pb: 0.9 (0.1-11)				Deshommes et al.[14]; Nour et al.[15]; Cartier et al.[22]
	Frequency for RDT consumption — %				70 (Figure 6a); 57.5-70 (Figure 6b)				-
	5min of flushing concentration[b] in LSL houses — μg Pb/L				Median soluble Pb: 10; Median (10th-95th percentile) particulate Pb: 0.2 (0.04-1.4)				Deshommes et al.[14]; Cartier et al.[22]
	Frequency for 5 min of flushing consumption — %				20 (Figure 6a); 17.5-30 (Figure 6b)				-
	1st flush concentration[c] in large buildings — μg Pb/L				Median soluble Pb: 51; Median (10th-95th percentile) particulate Pb: 20 (4-490)				Deshommes et al.[16]
	Frequency for 1st flush consumption — %				10 (Figure 6a); 0-25 (Figure 6b)				-
	RBA — %				Particulate Pb: 33; Dissolved Pb: 50				RBA evaluated with the *in vivo-in vitro* relationship by Drexler and Brattin,[20] using median IVBA from this study
DUST/SOIL	Soil + dust intake — g/d	0.085	0.135	0.135	0.135	0.100	0.090	0.085	Default IEUBK
	Soil/Dust ingestion weighting factor — % soil				40				Higher than default IEUBK (35) considering cold climate
	Soil concentration — μg Pb/g				33.78				Rasmussen et al.[25]
	Soil RBA — %				30				Default IEUBK
	Dust concentration — μg Pb bioavailable/g				52.47[d]				Rasmussen et al.[24] values, adjusted with the *in vivo-in vitro* relationship by Drexler and Brattin[20]
	Dust RBA — %				100				Dust concentration considers Pb bioavailability
AIR	Indoor Pb concentration — % outdoor	30	30	30	30	30	30	30	Default IEUBK
	Time spent outdoor — hr/d	1	2	3	4	4	4	4	Default IEUBK
	Outdoor air Pb concentration — μg Pb/m^3				0.0015				Health Canada[26]
	Ventilation rate — m^3/d	2	3	5	5	5	7	7	Default IEUBK
	Lung absorption — %				32				Default IEUBK
OTHER	Dietary Pb intake — μg Pb/d	2.26	1.96	2.13	2.04	1.95	2.05	2.22	Default IEUBK values agree with Canadian values[26,27]
	Maternal BLL — μg Pb/dL				1				Default IEUBK values agree with Canadian values[26]

[a]*2007-2008 Montreal summer sampling campaigns using random daytime sampling—RDT*[14,22] *(N=196; 2008 monitoring campaign not published), includes 27 samples performed using particulate stimulation samplings,*[14] *and 15 samples collected at high flow rate.*[15] [b]*From 2006-2008 Montreal summer sampling campaigns*[14,22] *(N=218; 2008 monitoring campaign not published).* [c]*From Deshommes et al.*[16] *using only results from taps dedicated to drinking water consumption (N=35.* [d]*52% RBA for dust deduced from the in vivo-in vitro relationship by Drexler and Brattin*[20] *and the geometric mean IVBA of 62%; then, to obtain the concentration of bioavailable Pb (μg Pb/g dust), the median concentration of bioaccessible Pb (63 μg Pb/g dust) was multiplied by its RBA% (52) and divided by its IVBA% (62).*

In this way, the RBA considered by IEUBK for soluble Pb remained at 50% (default value), and the RBA relative to particulate Pb was taken into account:

$$50\% \times Pb_{total,\mu g \cdot L^{-1}}$$
$$= 50\% \times Pb_{dissolved,\mu g \cdot L^{-1}} + (Pb_{particulate,\mu g \cdot L^{-1}} \times RBA_{\%})$$

Pb concentrations in dust, soil, and diet, as well as ingestion rates were population-specific.[23−27] In absence of data, the default IEUBK values were applied (Table 1).

RESULTS AND DISCUSSION

Lab-Generated Particles. IVBA% varied with the type of particle tested, in the following decreasing order: Pb(II) > R-brass > Y-brass > Pb(IV) > solder (Figure 1). Such results are quite comparable to the solubility of lab-generated particles reported after about 1 h at pH 1.2 in a simulated gastric fluid by Triantafyllidou et al.[13] This classification was independent of the average Pb content in the particles tested, which was evaluated at 1.7% for the Y-brass, 6.7% for the R-brass, 46% for the Pb(II) scale, 49% for the solder, and 84% for the Pb(IV) particles, the latter being quite highly bioaccessible (34−45%) under the testing conditions, although they are generally poorly soluble in drinking water.[28−30] The LSL deposits mainly composed of Pb carbonates were, not surprisingly, highly bioaccessible (95−96%), considering their high solubility in this distribution system that does not apply any corrosion control.[14] Pb(IV)- and Pb(II)-based scales can develop into LSLs, and therefore may be present at the tap. They can become detached by physical disturbances in the plumbing associated with consumers' water usage patterns (high flow rate, water hammer), and occasionally, but to a large degree, following a disinfectant change.[14,28−31] It must be noted that those two species of high Pb content, presented a significantly higher mean IVBA in mg Pb/g bulk particles (328−439) than other particles tested (7−57) (Figure 1). The brasses and the solder tested may represent more a widespread source of exposure to particulate Pb for the consumer, since these Pb-bearing materials are ubiquitous in PP. The relatively low bioaccessibility of the solder and the lower Pb content of brass devices should not be interpreted as constituting a lower risk of significant Pb ingestion compared to that of the Pb scales tested. In fact, the sustained and elevated release of particulate Pb resulting from the corrosion of brass devices and solders has been documented, and may represent a substantial source of chronic exposure for children attending school/daycare every day.[16,32,33]

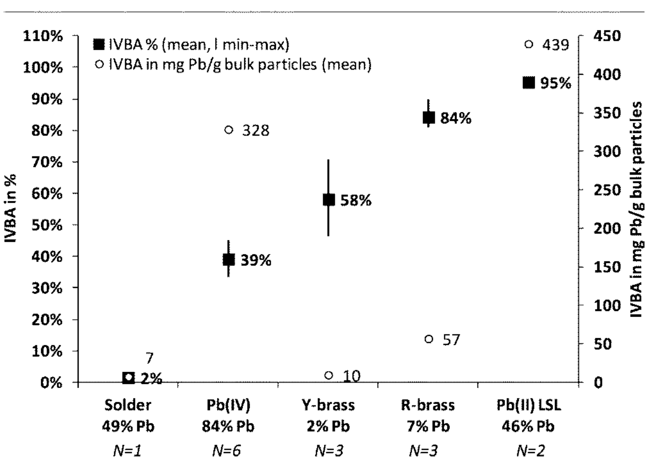


Figure 1. In vitro bioaccessibility (IVBA) for lab-generated particles. IVBA % on the left Y-axis (mean, min−max); mean IVBA in mg Pb/g bulk particles on the right Y-axis.

Field-Collected Particle Composition. Figure 2a shows the cumulative distributions (percentiles) of the main metals contents in the 65 sets of field particles tested. In about 90% of

dx.doi.org/10.1021/es2045585 | Environ. Sci. Technol. 2012, 46, 6269−6277

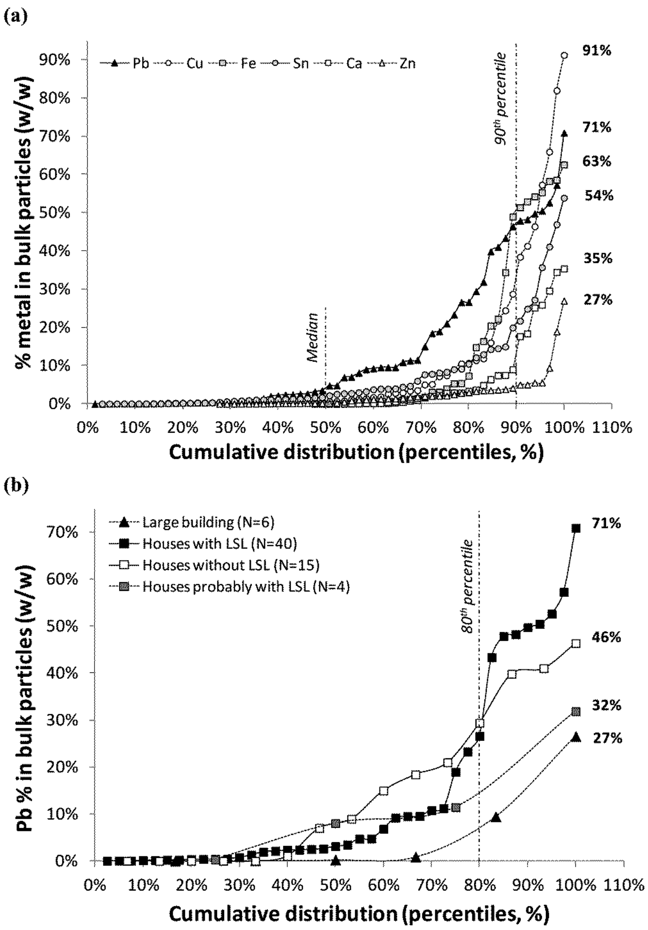


Figure 2. Cumulative distribution (percentiles, %) of the metal content (%) in the 65 sets of field-collected particles tested. (a) Metals % for all samples; (b) Pb % per type of building.

the samples, Pb was the main component present. A median of 4.7% and values up to 71% Pb were recorded in the bulk particles tested, and 43% of the sets contained more than the 8% Pb formerly allowed for plumbing devices. Tin was the second largest component of the samples, based on the median (2.2%). The dominant metals measured in the particles from the aerators were characteristic of PP (Cu, Pb, Sn, Zn), in agreement with the particulate Pb forms (brass and solders) reported in the tap water from these same sites.[14] Iron and calcium particle content was also significant, and may have come from deposits formed into the piping over time, specifically corroded galvanized iron piping in the case of Fe particles.[14] Overall, no significant difference ($p = 0.42$) was found between the Pb content of particles collected from homes with and without an LSL. However, there is clearly a higher Pb content in samples from LSL homes than from homes without an LSL above the 80th percentile of the Pb% distribution (Figure 2b). It may be incorrect to conclude from such trends that some LSLs can be a significant source of Pb particles, since the opposite trend was observed in the 50th to 80th percentile range. In fact, whether or not there was an LSL, 12/13 samples over the 80th percentile and 4/16 samples in the 50th−80th percentile range were high in Sn, suggesting solder, while 9/16 samples in the 50th−80th percentile range were high in Cu−Zn−Sn, suggesting that brass was the most likely source. Small, friable, Pb-rich deposits released from an LSL would not be retained by an aerator. Furthermore, they would likely be measured in the total Pb analysis during the digestion procedure. In general, the multimetal composition of the particles collected indicates that the PP (solder, brass), rather than the LSL, was the main source. For the samples with a high Fe content, higher Pb levels were found in homes with an LSL (0.2−0.8%) than in those without an LSL (0.01%), in agreement with prior findings.[14] These results suggest that, for the system studied, the absence of an LSL does not greatly influence exposure to Pb particles, since they originate mostly from the PP.

An aerator can trap a considerable amount of particles, making this area a significant reservoir of Pb. Among the 42 samples tested directly (i.e., one sample from one tap aerator), the bulk particle mass varied within 0.01−0.08 g, corresponding to 0.0009−15 mg total Pb (mean: 2.8 mg). Such Pb-bearing particles can dissolve during stagnation, or break down and break through the aerator mesh with sheer from flow over time, contributing to elevated Pb levels at the tap and consequently to consumer exposure.[13,22] An obvious way to limit potential exposure associated with these particles is to advise cleaning the aerator tap regularly, and to buy faucets in which the aerator can be easily removed.

Field-Collected Particle Bioaccessibility. Figure 3 presents the distribution of IVBA results from field-collected particles. The IVBA% was uniformly distributed between 1.5% and 100%, with a median of 41%. From this median IVBA, a median RBA of 33% could be deduced using the relationship proposed by Drexler and Brattin.[20] IVBA also varies quite uniformly in terms of mg of Pb bioaccessible per g of bulk particles between 0.02 and 82, as 64 of the samples are in this range. An extreme at 436 mg Pb/g was also measured, corresponding to the highest Pb content found in the field particle samples (71%). IVBA/g values for the field particles fall within the range of the values for the lab-generated particles, although they are a bit lower (median: 11 mg Pb/g). The lab-generated particles were all Pb-bearing, while the field-collected particles were composed of a mix of particles, only some of which contained Pb, which decreased the overall IVBA/g values. It is worth noting that lab-generated particles exhibiting the highest IVBA (>300 mg Pb/g) were Pb scales from LSLs, which were not represented in the field particles, as they are too small and friable to be retained by aerators.

The range of IVBA, whether in % or mg Pb/g, is quite broad and represents a correspondingly broad range of potential consumer exposures. As for the Pb content in particles, the IVBA was not significantly different in homes with and without an LSL (t test, $p > 0.5$, for IVBA% or IVBA/g). However, as noted previously, this lack of impact of the LSL is most likely explained by the nature of the particles tested, which originated mostly from the PP. In addition to Pb particles from this source, consumers living in homes with an LSL may be exposed to Pb particles released from LSL scale deposits. However, since particles released from Pb(II) and Pb(IV) scales are likely to be very small or colloidal, their contribution is taken into account in the total and dissolved Pb measurements at the tap.[14,31]

The samples were classified based on their dominant phase, which was defined as composing at least 15% of the total mass of the sample. Five dominant phase categories were identified, based on the appearance of the particles sampled and on the metal content and proportion in the particles tested: Ca, Fe, Cu−Pb−Sn−Zn, Cu−Pb−Sn, and Pb−Sn. Particles containing on average 27% Ca exhibited the highest IVBA: 32−100%, with

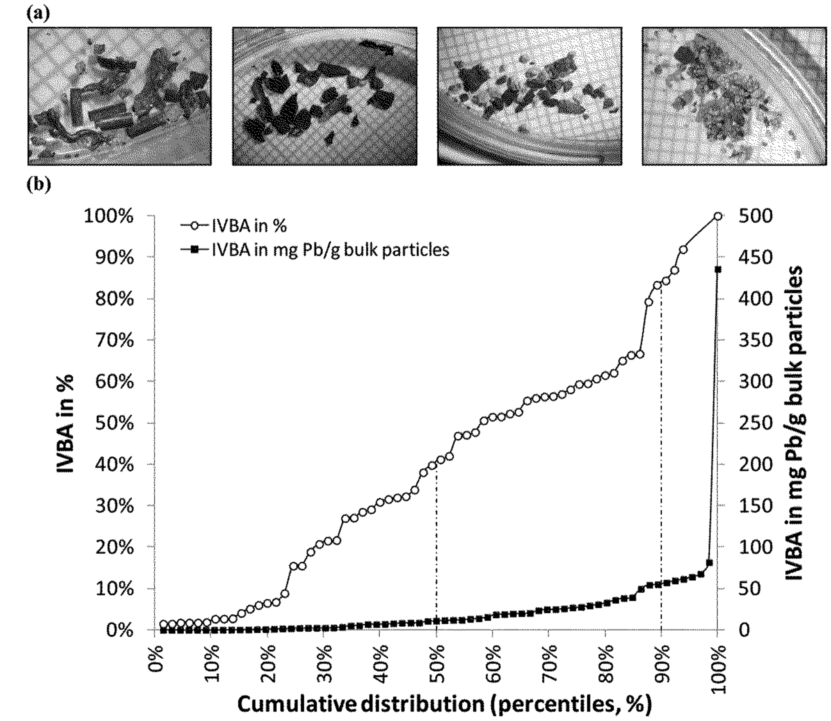


Figure 3. (a) Examples of field-collected particles. Note: each side of the squares = 1 mm; (b) Cumulative distribution (percentiles, %) of IVBA in the 65 sets of field-collected particles tested. Y-left axis: O-IVBA %; Y-right axis: ■-IVBA in mg Pb/g bulk particles.

a median of 59% (Figure 4). The median IVBA was comparable for the Fe (51%), the Cu−Pb−Sn (50%), and the Cu−Pb−Sn−Zn (47%) categories, while the upper values for the Cu−Pb−Sn category were lower. Finally, particles for the most part containing Pb/Sn solders had the lowest IVBA (median 5%). Moreover, the first twelve values of the IVBA distribution curve presented in Figure 3 (1.5−6%) correspond to samples composed exclusively (N = 9) or mostly of solders. The t test results comparing the Pb−Sn category and the other phase categories were all significant ($p < 0.0001$), while the other categories were not statistically different from one another ($p = 0.12−0.86$). On the basis of these observations, consumer exposure to particulate Pb is determined primarily by particle type, and strongly influenced by the presence of solders. Pb speciation in soil and dust particles has been shown to be a major predictor of their bioaccessibility, since Pb dissolution during digestion varies according to the mineral composition of the Pb particles.[18] By compiling their results from soils, the USEPA was able to generate an IVBA classification based on the dominant phases present in the soils tested: >75% for cerussite and Pb-Manganese oxide; 25−75% for Pb-Phosphate and PbO forms; and <25% for anglesite, galena, Fe−Pb species, and the remaining Pb-based oxides.[34] Finally, Rasmussen et al.[24] were able to predict the IVBA by identifying the dominant Pb species in the dust samples tested with X-ray Absorption Spectroscopy. However, for the field-collected particles tested in this study, IVBA differences were most significant between solders and other categories of particles. These results are consistent with trends measured with laboratory particles which reveal a medium to high IVBA% for brasses and typical LSL scales, while solders constitute the only type of Pb particle with a low IVBA%.

IVBA results for solder and Fe-based particles collected from the same aerator and separated by particle size are presented in Figure 5. Bioaccessibility increased from 1.5% for solder B

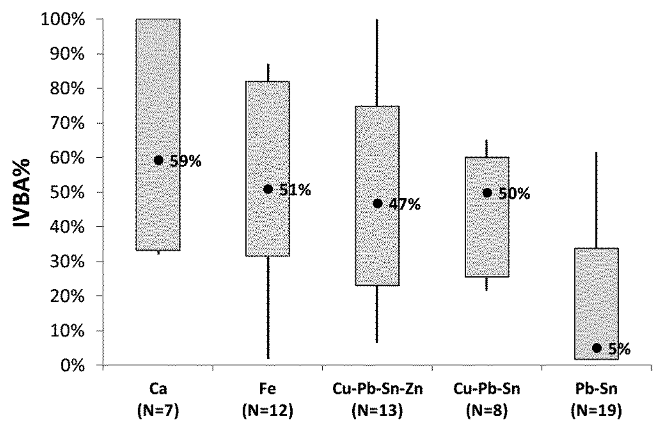


Figure 4. IVBA % per category of dominant phase (≥15% of the total mass of particles). Box-plot 10−90%, I min−max, ● median.

(diameter ≈ 3 mm) to 2.8% for sample D made up of 35 smooth, rounded solders about 0.5−1 mm in diameter (Figure 5a). Surprisingly, the much larger solder sample, A (~4 × 4 mm), exhibited the highest bioaccessibility (4.1%) although apparently with a much smaller surface to volume ratio. Differences in IVBA did not correspond to a higher Pb content, as it was quasi-constant in the samples (48−50%). However, the irregular shape and rough surface of sample A may actually provide a larger surface for acid attack than that of other samples that were rounded and smooth. In the case of Fe-based particles containing 0.24−0.45% Pb, IVBA% increased with decreasing particle size (+24%; Figure 5b). Although these investigations on size effects were limited considering the small amounts and the heterogeneity of the particles tested, it could be argued that the distribution presented in Figure 3 could underestimate the IVBA of smaller particulate Pb commonly found in tap water (>0.45 μm). These results are in agreement

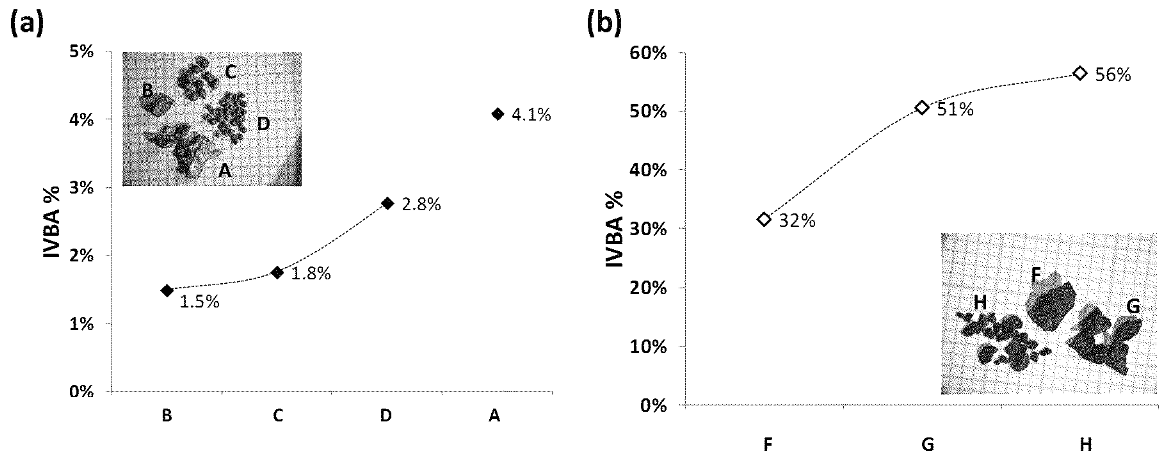


Figure 5. IVBA% per size of particles. Particles from the same aerator tap, from a house with an LSL. (a) Solders containing 48% Pb (A, B) and 50% Pb (C, D); (b) Fe corrosion particles containing 0.24−0.25% Pb (F, G) and 0.45% Pb (H). Note: each side of the squares = 1 mm.

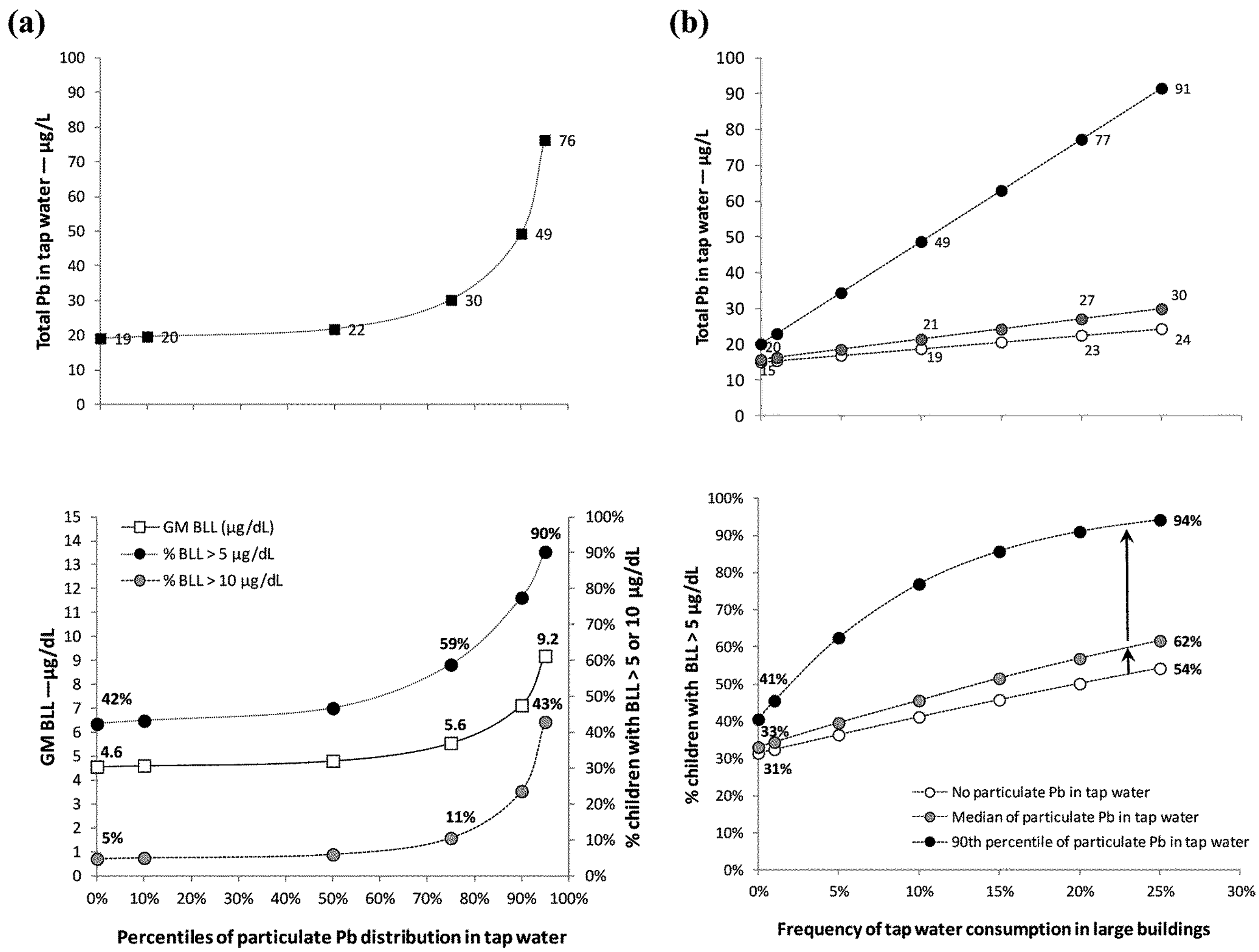


Figure 6. IEUBK simulations considering exposure from soil, dust, diet, air, and tap water. (a) Pb concentrations in tap water considered for exposure are a weighted mean of 70% RDT & 20% 5 min-flushing concentrations from homes with an LSL, and 10% 1st flush concentrations from large buildings − median dissolved Pb levels are applied (fixed), and particulate Pb is progressively increased from 0 to the 95th percentile of its distribution in tap water samples (X-axis) − resulting total Pb concentrations (dissolved Pb median plus particulate Pb) are indicated on the top; (b) Results with progressive increase of consumption frequency in large buildings (0−25%) considering exposition to median dissolved Pb levels in tap water samples plus: (i) no particulate Pb in tap water; (ii) the median of particulate Pb distribution in tap water samples; and (iii) the 90th percentile of particulate Pb distribution in tap water samples · when increasing the frequency of consumption in large buildings, the ratio of consumption frequency between RDT and 5 min-flushing concentrations is kept constant.

with prior results on soil/dust particles. The impact of particle size would be greatest for very small or colloidal particles (<2.4 μm, <63 μm), although the extent of this impact will be greatest for Pb phases with low solubility.[35−37] Conversely, our results do not indicate any Pb enrichment for the smallest fraction sizes.[38] This may relate to the nature of the particles from tap water, since their Pb content is determined prior to their detachment into tap water from scales or PP components. Finally, the 10 times higher IVBA for Pb−Fe particles as compared to solder particles shows that speciation is the driving factor of IVBA rather than the bulk particles' size.

IEUBK Simulations. The IEUBK model was used to estimate the impact of particulate Pb on the exposure of children aged 0.5−7. Soil, dust, air and diet exposures were adjusted to reflect typical Canadian values (Table 1), which are significantly lower than the default IEUBK settings, except for dust, which is comparable. Background dissolved Pb in tap water applied was determined as the weighted average of the median concentrations from three sampling campaigns conducted in households with LSL, and a sampling campaign conducted in a large building complex (Table 1). Using the median RBA (33%) measured from the particles collected from these same sites (field-collected particles), particulate Pb exposure was added to the background levels and used as the drinking water input as discussed in the Materials and Methods section. The use of a fixed median RBA value is justified given the wide and varying range of particulate Pb forms typically present in tap water and their sporadic presence.[14] Figure 6a represents the impact on BLLs of particulate Pb as a function of its measured distribution in tap water (0−95th percentile). The underlying scenario of drinking water Pb concentration is a weighted mean of 70% RDT samples from a house with an LSL, 20% 5-min flushing samples from a house with an LSL, and 10% first flush samples from large buildings. This scenario was selected to represent a conservative yet realistic estimate of exposure for a child drinking tap water (either directly or through water-based food or beverages), living in a house with an LSL and attending daycare or school. The estimated geometric mean (GM) BLL and the estimated fraction of children with BLL exceeding all thresholds are quite stable when concentrations of particulate Pb are lower than the median of the particulate Pb distribution (Figure 6a). However, the impact of particulate Pb becomes noticeable from the 75th percentile of the particulate Pb distribution, and considerable at the 90th and 95th percentiles. Specifically, the GM BLL increases from 4.6 μg/dL for no particulate Pb content, to 5.6 and 9.2 μg/dL for the 75th and 95th percentiles of particulate Pb, respectively. More strikingly, the estimated number of children with BLL > 10 μg/dL, which is the current health intervention guideline, increases from 5% for no particulate Pb content, to 11% and 43% for the 75th and 95th percentiles. The application of a lower BLL threshold at 5 μg/dL dramatically increases the estimated fraction of children exceeding the action level, to 42−90%. This illustrates the ramifications of the anticipated lowering of the BLL threshold, as the current 10 μg/dL threshold was recently recognized as no longer valid, considering the significant neurodevelopmental effects observed in children BLLs < 5 μg/dL.[1−4]

Finally, to assess the representativeness of these simulations, the modeled BLLs were compared to BLLs recently reported in Montreal. An adjusted GM of 1.90 μg/dL (95% CI: 1.59−2.27 μg/dL) was measured on 171 children aged 1−6 living in households with an LSL.[21] The IEUBK estimate of 4.6 μg/dL (without particulate Pb) significantly exceeds the measured BLLs. Several factors explain this difference. The BLL study was completed in fall and winter during which time Pb concentrations at the tap in households with an LSL were extremely low (median 4.0 μg/L), due to both the type of homes sampled and the low water temperature (1.4 °C in December).[21,39] The total Pb concentrations used in our simulations for households with an LSL, based on summer samples, were much higher with median values of 20 and 11 μg/L for RDT and 5 min flushing samples respectively. Although a different pool of houses was sampled, it is evident that higher water temperatures are associated with higher Pb tap concentrations. Considering the amplitude of the variations of Pb concentrations at the tap, a short-term exposure model would be preferable for predicting seasonal BLLs.[40] Moreover, our simulations consider 10% of the tap water consumption in a problematic large building complex. The IEUBK estimate without this contribution (70% · RDT and 30% · 5-min flushing, LSL households, no particulate Pb) decreases to 4.1 μg/dL. The remaining gap between measured and modeled BLLs may also reflect the differences between the water intakes used. Our IEUBK simulations consider that children drink a significant volume of tap water daily, as determined by the local health authority (742−1000 mL/d),[23] whereas children selected in the BLL study apparently consumed less tap water (295−385 mL/d).[21] Selecting higher consumption values is desirable to produce conservative yet realistic estimates of population exposure and to protect susceptible populations.[1] Finally, our simulations considered children aged 0.5−7. As expected, the highest BLLs were predicted for children under 3. The BLL study was mostly conducted on children aged 3−6 (62%), who are projected to show lower BLLs.

The significant BLL increases observed in Figure 6a, resulting from the particulate Pb exposure of children consuming 10% of their water in large buildings such as a school, are driven by the distribution of particulate Pb concentrations found in these large buildings. As shown in Table 1, the large building complex studied presents significantly higher particulate Pb than residences with an LSL, and are clearly problematic buildings. Figure 6b shows the impact of increasing the fraction of tap water consumed in such buildings, reflecting the time spent out of the home during daycare or school. The proportion of tap water consumed in large buildings was increased progressively from 0 to 25%. The importance of greater consumption of tap water from these large buildings is clearly shown by the fraction of children with BLLs > 5 μg/dL, which rose from 31% to 54% when the consumption increased to 25%, considering no exposure to particulate Pb (exposure to: soluble Pb-tap water; Pb-soil; Pb-dust; Pb-diet; Pb-air). If median particulate Pb concentrations are added to the background soluble Pb exposure, then the fraction of children exceeding the threshold increased from 33 to 62%. If a higher value is used, such as the 90th percentile of particulate Pb concentrations, then 41 to 94% of children are expected to exceed the 5 μg/dL threshold. These results suggest that particulate Pb can significantly contribute to Pb exposure at the tap, to the same extent as from Pb released from LSLs, especially in light of the anticipated reduction of the BLL threshold. The contribution of particulate Pb at the sites studied was dominated by the fraction of water consumed in these large buildings and the selection of the percentile concentration. Our results suggest that large buildings with elevated particulate Pb should be identified in order to lower Pb exposure from tap water. It would appear to be a matter of urgency, therefore, to conduct sampling campaigns in large buildings using protocols designed to detect both soluble and particulate Pb, so that critical situations can be identified and mitigated.

ASSOCIATED CONTENT

* Supporting Information

Details on the IVBA protocol and on the IEUBK simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel: (+1) 514-340-4711 (2236), e-mail: elise.deshommes@polymtl.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the support of Laurent Laroche, José-Maria Mora, Ecaterina Bologa, and André Boisvert (City of Montreal); Sébastien Sauvé, Thierry Maris, and Paul Fayad (University of Montreal); Manon Leduc, the CM2 laboratory, Mireille Blais and Julie Philibert (École Polytechnique de Montréal), Marc Edwards and Simoni Triantafyllidou (Virginia Tech); Technicians from the INSPQ; They also acknowledge the financial support from the CWN.

REFERENCES

(1) European Commission. Lead Standard in Drinking Water; Scientific Committee on Health and Environmental Risks SCHER: Brussels, Belgium, 2011; p 12.

(2) Codex Alimentarius Commission. Working Document for Information and Use in Discussions Related to Contaminants and Toxins in the GSCTFF; Food and Agriculture Organization of the United Nations and World Health Organization: The Hague, The Netherlands, 2011; p 90.

(3) Lanphear, B. P.; Hornung, R.; Ho, M.; Howard, C. R.; Eberle, S.; Knauf, K. Environmental lead exposure during early childhood. J Pediatr. 2002, 140 (1), 40−47.

(4) Jusko, T. A.; Henderson, C. R., Jr.; Lanphear, B. P.; Cory-Slechta, D. A.; Parsons, P. J.; Canfield, R. L. Blood lead concentrations <10 microg/dL and child intelligence at 6 years of age. Environ. Health Perspect. 2008, 116 (2), 243−248.

(5) Lanphear, B. P.; Hornung, R.; Khoury, J.; Yolton, K.; Baghurst, P.; Bellinger, D. C.; Canfield, R. L.; Dietrich, K. N.; Bornschein, R.; Greene, T.; Rothenberg, S. J.; Needleman, H. L.; Schnaas, L.; Wasserman, G.; Graziano, J.; Roberts, R. Low-level environmental lead exposure and children's intellectual function: An international pooled analysis. Environ. Health Perspect. 2005, 113 (7), 894−899.

(6) Brown, M. J.; Raymond, J.; Homa, D.; Kennedy, C.; Sinks, T. Association between children's blood lead levels, lead service lines, and water disinfection, Washington, DC, 1998−2006. Environ. Res. 2011, 111 (1), 67−74.

(7) Schock, M. R. In Distribution systems as reservoirs and reactors for inorganic contaminants (Chapter 6), 21st Century, Distribution System Water Quality Challenges, American Water Works Association, Denver, Colorado, USA, 2005; pp 105−140.

(8) Sandvig, A.; Kwan, P.; Kirmeyer, G.; Maynard, B.; Mast, D.; Rhodes Trussell, R.; Trussell, S.; Cantor, A.; Prescott, A. Contribution of Service Line and Plumbing Fixtures to Lead and Copper Rule Compliance Issues; 91229; American Water Works Association Research Foundation: Denver, Colorado, USA, 2008; p 523.

(9) Triantafyllidou, S.; Edwards, M. Lead (Pb) in tap water and in blood: implications for lead exposure in the United States (in press). Crit. Rev. Environ. Sci. Technol. 2011, 41, (20); DOI:10.1080/10643389.2011.556556.

(10) Miranda, M. L.; Kim, D.; Hull, A. P.; Paul, C. J.; Galeano, M. A. O. Changes in blood lead levels associated with use of chloramines in water treatment systems. Environ. Health Perspect. 2007, 115 (2), 221−225.

(11) Edwards, M.; Triantafyllidou, S.; Best, D. Elevated blood lead levels in young children due to lead-contaminated drinking water: Washington: DC, 2001−2004. Environ. Sci. Technol. 2009, 43 (5), 1618−1623.

(12) Lytle, D. A.; Schock, M. R.; Dues, N. R.; Clark, P. J. Investigating the preferential dissolution of lead from solder particulates. J. Am. Water Works Assoc. 1993, 85 (7), 104−110.

(13) Triantafyllidou, S.; Parks, J.; Edwards, M. Lead particles in potable water. J. Am. Water Works Assoc. 2007, 99 (6), 107−117.

(14) Deshommes, E.; Laroche, L.; Nour, S.; Cartier, C.; Prévost, M. Source and occurrence of particulate lead in tap water. Water Res. 2010, 44 (12), 3734−3744.

(15) Nour, S.; Prévost, M.; Cartier, C.; Laroche, L.; Edwards, M. In Impact of sampling flow rate, flushing, and faucet aerator on dissolved and particulate lead concentrations at consumer tap, American Water Works Association-Water Quality Technology Conference Charlotte, North Carolina, USA, 2007; p 9.

(16) Deshommes, E.; Nour, S.; Richer, B.; Cartier, C.; Prévost, M. POUs in large buildings: Lead removal and water quality. J. Am. Water Works Assoc. 2012, 104 (4), E282−E297.

(17) Ruby, M. V.; Schoof, R.; Brattin, W.; Goldade, M.; Post, G.; Harnois, M.; Mosby, D. E.; Casteel, S. W.; Berti, W.; Carpenter, M.; Edwards, D.; Cragin, D.; Chappell, W. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. Environ. Sci. Technol. 1999, 33 (21), 3697−3705.

(18) Deshommes, E.; Tardif, R.; Edwards, M.; Sauvé, S.; Prévost, M. Experimental determination of the oral bioavailability and bioaccessibility of lead particles (Submitted). Toxicol. Environ. Chem. 2012.

(19) Weis, C. P.; LaVelle, J. M. Characteristics to consider when choosing an animal model for the study of lead bioavailability. Chem. Spec. Bioavailab. 1991, 3 (314), 113−119.

(20) Drexler, J. W.; Brattin, W. J. An in vitro procedure for estimation of lead relative bioavailability: with validation. Human Ecol. Risk Assess. 2007, 13 (2), 383−401.

(21) Institut National de Santé Publique du Québec (INSPQ). Étude de l'Impact de la Contamination par le Plomb de l'Environnement Résidentiel sur la Plombémie des Jeunes Enfants; Santé Canada, Direction de la Santé Environnementale et de la Toxicologie, 2011; p 456.

(22) Cartier, C.; Laroche, L.; Deshommes, E.; Nour, S.; Richard, G.; Edwards, M.; Prévost, M. Investigating dissolved lead at the tap using various sampling protocols. J. Am. Water Works Assoc. 2011, 103 (3), 55−67.

(23) Beausoleil, M.; Brodeur, J. Le Plomb dans l'Eau Potable sur L'Île de Montréal. Etat de Situation et Évaluation des Risques à la Santé; Agence de la santé et des services sociaux de Montréal. Direction de Santé Publique: Montréal, Québec, Canada, 2007; p 59.

(24) Rasmussen, P. E.; Beauchemin, S.; Chenier, M.; Levesque, C.; MacLean, L. C. W.; Marro, L.; Jones-Otazo, H.; Petrovic, S.; McDonald, L. T.; Gardner, H. D. Canadian house dust study: Lead bioaccessibility and speciation. Environ. Sci. Technol. 2011, 45 (11), 4959−4965.

(25) Rasmussen, P. E.; Subramanian, K. S.; Jessiman, B. J. A multi-element profile of housedust in relation to exterior dust and soils in the city of Ottawa, Canada. Sci. Total Environ. 2001, 267, 125−140.

(26) Health Canada. Draft human health state of the science report on lead, 2011; p 87.

(27) Ljung, K.; Palm, B.; Grandér, M.; Vahter, M. High concentrations of essential and toxic elements in infant formula and infant foods • A matter of concern. Food Chem. 2011, 127 (3), 943−951.

(28) Lytle, D. A.; Schock, M. R. Formation of Pb(IV) oxides in chlorinated water. J. Am. Water Works Assoc. 2005, 97 (11), 102−114.

(29) Xie, Y.; Wang, Y.; Giammar, D. E. Impact of chlorine disinfectants on dissolution of the lead corrosion product PbO_2. Environ. Sci. Technol. 2010, 44 (18), 7082−7088.
(30) Xie, Y.; Wang, Y.; Singhal, V.; Giammar, D. E. Effects of pH and carbonate concentration on dissolution rates of the lead corrosion product PbO_2. Environ. Sci. Technol. 2010, 44 (3), 1093−1099.
(31) McNeill, L. S.; Edwards, M. Importance of Pb and Cu particulate species for corrosion control. J. Environ. Eng. 2004, 130 (2), 136−144.
(32) Boyd, G. R.; Pierson, G. L.; Kirmeyer, G. J.; Britton, M. D.; English, R. J. Lead release from new end-use plumbing components in Seattle Public Schools. J. Am. Water Works Assoc. 2008, 100 (3), 105−114.
(33) Boyd, G. R.; Pierson, G. L.; Kirmeyer, G. J.; English, R. J. Lead variability testing in Seattle Public Schools. J. Am. Water Works Assoc. 2008, 100 (2), 53−64.
(34) United States Environmental Protection Agency (USEPA) Estimation of Relative Bioavailability of Lead in Soil and Soil-Like Materials Using in Vivo and in Vitro Methods; OSWER 9285.7−77; Office of Solid Waste and Emergency Response: Washington, DC, USA, 2007; p 74.
(35) Ruby, M. V.; Davis, A.; Kempton, J. H.; Drexler, J. W.; Bergstrom, P. D. Lead bioavailability: dissolution kinetics under simulated gastric conditions. Environ. Sci. Technol. 1992, 26 (6), 1242−1248.
(36) Medlin, E. A. An in vitro method for estimating the relative bioavailability of lead in humans (Masters). University of Colorado: Boulder, Colorado, USA, 1997.
(37) Mercier, G.; Duchesne, J.; Carles-Gibergues, A. A new in vitro test to simulate gastric absorption of copper, lead, tin and zinc from polluted soils. Environ. Technol. 2002, 23 (2), 121−133.
(38) Juhasz, A. L.; Weber, J.; Smith, E. Impact of soil particle size and bioaccessibility on children and adult lead exposure in pen-urban contaminated soils. J. Hazard. Mater. 2011, 186 (2−3), 1870−1879.
(39) Nour, S.; Prévost, M. In Developing a comprehensive strategy to reduce lead at the tap. Health study: tap water lead concentration results. Workshop CWN on Lead in Drinking Water: Health Impacts, Monitoring and Control, Montréal, Québec, Canada, 2011; p 28.
(40) Donahue, J. M., Mendez, W., Shapiro, A., Modeling the Impact of Short-term Lead Exposure on Blood Lead Levels In Young Children (Poster). Society of Toxicology Annual Meeting, Washington D.C., 2011.

dx.doi.org/10.1021/es2045585 | Environ. Sci. Technol. 2012, 46, 6269−6277